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0401838.8

28 JAN 2004

3. Full name, address and postcode of the or of each applicant (*underline all surnames*)

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Patents ADP number (*if you know it*)

8147845001

If the applicant is a corporate body, give the country/state of its incorporation

4. Title of the invention

Improved Agricultural Compositions

5. Name of your agent (*if you have one*)

J. A. KEMP & CO.

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Patents ADP number (*if you know it*)

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11. I/We request the grant of a patent on the basis of this application.

Signature(s)

J.A. KEMP & CO.

Date 28 January 2004

12. Name, daytime telephone number and e-mail address, if any, of person to contact in the United Kingdom

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DUPLICATE

-1-

IMPROVED AGRICULTURAL COMPOSITIONS

The present invention relates to compositions suitable for use in agriculture, horticulture and veterinary medicine.

5 It is well known that many of the active ingredients of veterinary, agricultural and horticultural compositions such as herbicides and insecticides are adversely affected by UV light. Such organic compounds have a tendency to degrade or decompose under the influence of UV light either to inactive compounds or compounds which have an adverse effect upon the area being treated. As a result it is
10 necessary to store these products in special containers which do not allow the penetration of UV light. Otherwise the shelf life of the product is too short.

In our GB Application No. 0312703.2 we disclose that the adverse effects of UV light on such organic compounds can be reduced and/or eliminated by incorporating in the composition titanium dioxide and/or zinc oxide which has been
15 doped with a second element and/or reduced zinc oxide. In other words by incorporating this specific oxide in the formulation it is possible to dispense with the use of special containers and/or extend the life of the product. In addition its presence enables the user to use less of the product. The application thus describes a composition suitable for veterinary, agricultural or horticultural use which comprises
20 at least one organic veterinarally, agriculturally and/or horticulturally active compound, and titanium dioxide and/or zinc oxide which has been doped with a second element and/or reduced zinc oxide as well as a method for treating a veterinary, agricultural or horticultural species at a locus which comprises treating the locus with such a composition.

25 While any reduction in the loss of UV absorption is an advantage, it is generally desirable that the presence of the oxide should reduce the rate of UV absorption by an amount of at least a 5%, preferably at least 10%, more preferably at least 15%, especially at least 20% and most preferably at least 40%.

It has now been found, according to the present invention, that the way in
30 which the oxide is doped has a material effect on the efficacy of the oxide. Indeed it

has now been appreciated that it is important that if the oxide is to be really effective there must be dopant on its surface which can interact with the component of the composition to be protected. For example if, in a two phase composition, the oxide is present in the aqueous phase and the component to be protected is in the organic phase there is little interaction because of the phase boundary. Thus the free radicals generated by degradation of the component cannot contact the dopant without moving from one phase to another. Although existing methods for doping in the bulk will normally also result in some dopant in or on the surface of the particle, it is possible according to the present invention to use materials which are only surface doped i.e. where there is dopant only in or on the surface of the particle. In one embodiment such materials may be used in a single phase aqueous formulation. Accordingly the present invention provides (although not dependent on the above theory) a composition suitable for veterinary, agricultural or horticultural use which comprises at least one organic veterinarily, agriculturally and/or horticulturally active compound, and titanium dioxide and/or zinc oxide which has been doped at least in or on a surface thereof with one or more other elements, typically with one i.e. with only a second element. Where the particle has been bulk doped there will, in general, be dopant throughout the particle. On the other hand, where the particle has been "surface doped" (i.e. the dopant is only in or on the surface) there will be a concentration gradient such that the ratio of dopant atoms to titanium or zinc atoms at the surface or outmost "skin" of the particle is greater than the ratio in the core or centre where it may be zero.

It will be appreciated that although it will normally be the case that the bulk dopant will be the same element as the or each surface dopant (for simplicity of preparation), this need not necessarily be the case. (Of course with reduced zinc oxide there is no bulk dopant.) By this means it is possible, for example, to modify the colour of the particles. Suitable dopants for the oxide particles include manganese, which is especially preferred, e.g. Mn^{2+} but also Mn^{3+} , vanadium, for example V^{3+} or V^{5+} , chromium and iron but other metals which can be used include nickel, copper, tin, especially Sn^{4+} , aluminium, lead, silver, zirconium, zinc, cobalt,

especially Co^{2+} , gallium, niobium, for example Nb^{5+} , antimony, for example Sb^{3+} , tantalum, for example Ta^{5+} , strontium, calcium, magnesium, barium, molybdenum, for example Mo^{3+} , Mo^{5+} or Mo^{6+} as well as silicon. These metals can be incorporated singly or in combinations of two or three or more. It will be appreciated that for
5 effective bulk doping the size of the ion must be such as can readily be inserted into the crystal lattice of the particle. For this purpose Mn^{3+} , vanadium, chromium and iron are generally the most effective; the ionic size of Mn^{2+} is much larger than that of Ti^{4+} and so there is little probability of ionic diffusion of Mn^{2+} into the TiO_2 crystal lattice. On the other hand there is no such size limitation for the elements used in
10 surface doping; preferred surface dopants include manganese, eg. as Mn^{2+} , cerium, selenium, chromium, vanadium and iron.

The optimum total amount of the second component on, and, if present in, the particle may be determined by routine experimentation but it is preferably low enough so that the particles are minimally coloured. Amounts as low as 0.1 mole %
15 or less, for example 0.05 mole %, or as high as 1 mole % or above, for example 5 mole % or 10 mole %, can generally be used. Typical concentrations are from 0.5 to 2 mole % by weight. The mole ratio of dopant to host metal on the surface is typically from 2-25:98-75, usually 5:20:95-80 and especially 8-15:92-85. The amount of dopant at the surface can be determined by, for example, X-ray
20 Photoelectron Spectroscopy (XPS).

The surface-doped particles can be obtained by any one of the standard processes for preparing such doped oxides and salts. These include techniques such as those described below. It will be appreciated that the dopant need not necessarily be present as an oxide but as a salt such as a chloride or a salt of an oxygen-
25 containing anion such as perchlorate or nitrate. However bulk doping techniques will generally result in some surface doping as well and these techniques can be used in the present invention. Such techniques include a baking technique by combining particles of a host lattice (TiO_2/ZnO) with a second component in the form of a salt such as a chloride or an oxygen-containing anion such as a perchlorate or a nitrate, in
30 solution or suspension, typically in solution in water, and then baking it, typically at a

temperature of at least 300°C. Other routes which may be used to prepare the doped materials include a precipitation process of the type described in J. Mat. Sci. (1997) 36, 6001-6008 where solutions of the dopant salt and of an alkoxide of the host metal (Ti/Zn) are mixed, and the mixed solution is then heated to convert the alkoxide to the oxide. Heating is continued until a precipitate of the doped material is obtained. Further details of preparation can be found in WO 00/60994 and WO 01/40114.

It will be appreciated that such baking techniques and the like will result in dopant in the surface forming part of the crystal lattice while in other techniques the dopant will merely be adsorbed, or remain as a separate layer, on the particle surface. It is thought likely that if the dopant is to quench internally generated free radicals then it needs to be in the crystal lattice.

The rutile form of titania is known to be less photoactive than the anatase form and is therefore preferred. Zinc oxide can be in the form of reduced zinc oxide particles (i.e. particles which possess an excess of zinc ions relative to the oxygen ions).

Doped TiO₂ or doped ZnO may be obtained by flame pyrolysis or by plasma routes where mixed metal containing precursors at the appropriate dopant level are exposed to a flame or plasma to obtain the desired product.

Further discussion details of such particles can be found in WO 99/60994.

The oxide particles used in the present invention may have an inorganic or organic coating. For example, the particles may be coated with oxides of elements such as aluminium, zirconium or silicon, especially silica or, for example, aluminium silicate. The particles of metal oxide may also be coated with one or more organic materials such as polyols, amines, alkanolamines, polymeric organic silicon compounds, for example, $\text{RSi}[\{\text{OSi}(\text{Me})_2\}_x\text{OR}^1]_3$ where R is C₁-C₁₀ alkyl, R¹ is methyl or ethyl and x is an integer of from 4 to 12, hydrophilic polymers such as polyacrylamide, polyacrylic acid, carboxymethyl cellulose and xanthan gum or surfactants such as, for example, TOPO. If desired the surface doping can be carried out by a coating technique either separately or in combination with the inorganic or organic coating agent. Thus for example the undoped oxide can be coated with, say,

manganese oxide along with an organic or inorganic coating agent such as silica.. It is generally unnecessary to coat the oxide particles to render them hydrophilic so that for the aqueous phase the particles can be uncoated. However if the particles are to be in the organic or oily phase their surface needs to be rendered hydrophobic or oil-dispersible. This can be achieved by the application directly of, for example, a suitable hydrophobic polymer or indirectly by the application of a coating, for example of an oxide such as silica (which imparts a hydrophilic property) to which a hydrophobic molecule such as a metal soap or long chain (e.g. C_{12} - C_{22}) carboxylic acid or a metal salt thereof such as stearic acid, a stearate, specifically aluminium stearate, aluminium laurate and zinc stearate.

It should be understood that the term "coating" is not to be construed as being limited to a complete covering. Indeed it is generally beneficial for the coating not to be complete since the coating can act as a barrier to the interaction of the free radicals with the dopant on or in the surface of the particle. Thus it is preferred that the coating should be discontinuous where maximum scavenging effect is desired. However it will be appreciated that dopant on the surface can still act to quench free radicals generated within the particle in which case the coating can be continuous.. Since coatings of silanes and silicones which can be polymeric or short chain or monomeric silanes are generally continuous these are generally less preferred. Thus coating with an inorganic oxide is generally preferred since these generally do not result in a complete coating on the surface of the particles.

Typical coating procedures include the deposition of silica by mixing alkali such as ammonium hydroxide with an orthosilicate, such as tetraethylorthosilicate, in the presence of the particle. Alternatively the particle can first be coated with a silane such as (3-mercaptopropyl) trimethoxy silane (MPS) and then silicate e.g. sodium silicate is added. The silane attaches to the particle surface and acts as a substrate for the silicate which then polymerises to form silica. Similar techniques can be used for other inorganic oxides.

The average primary particle size of the particles is generally from about 1 to 200 nm, for example about 1 to 150 nm, preferably from about 1 to 100 nm, more

preferably from about 1 to 50 nm and most preferably from about 20 to 50 nm. Since the scavenging effect is believed to be essentially catalytic it is desirable that the particles are as small as possible to maximise their surface area and hence the area of doped material on the surface. This small size has the advantage that less dopant is
5 needed which has the consequential advantage that any colouring effect caused by the dopant is reduced.

Where particles are substantially spherical then particle size will be taken to represent the diameter. However, the invention also encompasses particles which are non-spherical and in such cases the particle size refers to the largest dimension.

10 The compositions of the present invention can be single phase, either aqueous or oily or multiphase. Typical two-phase compositions comprise oil-in-water or water-in-oil formulations. For single phase compositions the oxide particles must of course be dispersible in that phase. Thus the particles are desirably hydrophilic if the composition is aqueous or hydrophobic if the composition is oil-based. However it
15 may be possible to disperse untreated TiO_2 in the oily phase by appropriate mixing techniques. For two or multi-phase compositions the particles must be present in the phase containing the ingredient (or one of those ingredients) to be protected. It can, though, be desirable for the particles to be present in both aqueous and oily phases even if no ingredients which are to be protected are present in one of those phases.
20 Desirably, the weight ratio of the water-dispersible particles to the oil-dispersible particles is from 1:4 to 4:1, preferably from 1:2 to 2:1 and ideally about equal weight proportions.

The present invention is applicable to any composition intended for agricultural or horticultural use which contains an organic active ingredient as well as
25 to veterinary compositions containing an organic active ingredient, generally for topical application. Generally the active ingredient will be a biocide but it can be, for example, a plant growth promoter or regulator. Thus the compositions of the present invention are typically herbicides, fungicides, insecticides, bactericides, acaricides, molluscicides, miticides or rodenticides, which can be broad spectrum or selective.
30 The present invention is particularly useful for fast knockdown insecticides which are

badly affected by UV light. Veterinary compositions can take the form of, for example, antiseptic or wound healing preparations.

The compositions of the present invention can also be formulated for household use as with, for example, insecticides and rodenticides. Accordingly, the present invention also provides a composition suitable for household use which comprises at least one organic biocide and titanium dioxide and/or zinc oxide which has been doped with a second element and/or reduced zinc oxide.

The compositions of the present invention can contain any of the organic active ingredients currently employed for such compositions.

Suitable herbicides which can be used in the present invention include triazines, amides, in particular haloacetanilides, carbamates, toluidines (dinitroanilines), ureas, plant growth hormones, in particular phenoxy acids and diphenyl ethers. Thus herbicides which may be used include phenoxy alkanoic acids, bipyridiniums, benzonitriles with phthalic compounds, dinitroanilines, acid amides, carbamates, thiocarbamates, heterocyclic nitrogen compounds including triazines, pyridines, pyridazinones, sulfonylureas, imidazoles and substituted ureas as well as halogenated aliphatic carboxylic acids, some inorganic and organic materials and derivatives of biologically important amino acids. Specific herbicides which can be used in the present invention include 2,4-dichlorophenoxyacetic acid (2,4-D) and 2, 4, 5-trichlorophenoxyacetic acid (2, 4, 5-T). Suitable triazines include 2-chloro-, 2-methylthio-, 2-methoxy-4,6-bis- (alkylamino)-s-triazines as well as some 2-azido-substituted triazines. Typical herbicidal ureas include monuron (3-p-chlorophenyl)-1,1-dimethylurea) as well as diuron, neburon, fenuron and chloroxuron. Suitable carbamates include N-phenylcarbamate and isopropyl carbanilate (propham) and substituted derivatives thereof including isopropyl m-chlorocarbanilate (chlorpropham) as well as barban, swep, dichlormate and terbutol. Suitable thiocarbamates include EPTC, metham, vernolate, CDEC, pebulate, diallate, triallate, butylate, molinate, cycloate, thiobencarb and ethiolate. Suitable amide herbicides include solan, dicryl, propanil, dipehamid, propachlor, alachlor, CDAA, naptalam, butachlor, prynachlor and napropamide. Suitable chlorinated aliphatic acids include

trichloroacetic acid (TCA), dalapon and 2,2,3-trichloropropionic acid. Suitable chlorinated benzoic acids include chloramben, DCPA, dicamba, dichlobenil and 2,3,6-TBA. Phenolic herbicides which can be used include bromoxynil, ioxynil, DNOC and dinoseb. Suitable dinitroanilines which can be used include benefin, trifluralin, nitralin, oryzalin, isopropalin, dinitramine, fluchloralin, profluralin and butralin. Suitable bipyridinium herbicides include diquat and paraquat salts and derivatives thereof.

Suitable insecticides which can be used in the present invention include nicotinoids, rotenoids, derivatives of the seeds of sabadilla and the plant ryania speciosa and pyrethroids as well as organochlorine insecticides, organophosphorus insecticides, carbamate insecticides and various insect growth regulators.

Suitable nicotinoids include nicotine sulfate and imidocloprid. The pyrethroids constitute a large group of insecticides most of which are now synthetic including resmethrin, phenothrin, cyphenothrin, empenthrin, prallethrin, permethrin, cypermethrin, alpha cypermethrin, tetramethrin and delta tetramethrin, including their isomers, especially optical isomers along with derivatives of these. Suitable organochlorine insecticides include DDT (dichlorodiphenyltrichloroethane) along with methoxychlor and perthane, as well as lindane, toxaphene, chlordane, heptachlor, aldrin, dieldrin and endrin. Suitable organophosphorus insecticides include phosphoric acid and phosphorothioic acid anhydrides, aliphatic phosphorothioate esters along with phenyl phosphorothioate esters, phenyl phosphorodithioate esters, phosphonothioate esters of phenols, vinyl phosphates, phosphorothioate esters of heterocyclic enols and of s-methyl heterocycles. Of these specific mention can be made of parathion, methyl parathion, dicapthion, chlorthion, fenitrothion, fenthion and fensulfothion along with fenchlorphos, cyanophos, propafos and temephos. Suitable carbamate insecticides which can be used include carbaryl, carbofuran, propoxur, dioxacarb, bendiocarb, mexacarbate, isoprocarb and ethiofencarb. Suitable acaricides include chlorfenethol, chlorobenzilate, dicofol, tetradifon, sulphenone, ovex, propargite, cyhexatin and dienochlor.

Some of the insecticides given above are suitable for killing rodents but other

rodenticides which can be used include acute rodenticides and chronic poisons include anticoagulants; these can be stomach poisons, contact poisons or fumigants. Such anticoagulants include dicoumarol, warfarin, coumatetraly, coumachlor, difenacoum, brodifacoum, bromadiolone, pindone, diphacinone and
5 chlorophacinone.

Insecticides which can be used in the compositions of the present invention can also be in the form of microbial agents since insects are attacked by many pathogens. These include bacterial agents, in particular bacillus microorganisms, especially bacillus thuringiensis (b.t.) strains such as b.t. aizawa, israelensis, kurstaki
10 and tenebrionis, fungal agents, protozoa and viruses.

Suitable fungicides which can be used in the compositions of the present invention include elements such as sulphur, copper, mercury and tin along with thiocarbamate and thiurame derivatives, phthalimides and trichloromethylthiocarboximides, aromatic hydrocarbons and dicarboximides.
15 Specific examples include ferbam, ziram, thiram, zineb, maneb and mancozeb as well as dimethylthiocarbamates and ethylene bis-dithiocarbamates. Other useful fungicides include captan, folpet, captafol and dichlofluanid. Suitable aromatic hydrocarbons include quintozone, dinocap, chloroneb, dichloran, dichlone and chlorothalonil along with oxazolidinediones such as vinclozolin, chlozolate,
20 hydantoin such as iprodione and succinimide such as procymidone. Other fungicides which can be used include guanidine salts such as dodine, quinones such as dithianon, quinoxalines such as chinomethionat, pyridazines such as diclomezine, thiadiazoles such as etridiazole, pyrroles such as fenpiclonil, quinolines such as ethoxyquin and triazines such as anilazine. Other fungicides which can be used
25 include mitochondrial respiration inhibitors which are generally carboxanilides including carbox, oxycarboxin, flutolanil, fenfuram, mepronil, methfuroxam and metsulfovax. Further fungicides which can be used include microtubuline polymerization inhibitors including thiabendazole, fuberidazole, carbendazim, benomyl and thiophanate methyl. Other suitable fungicides include inhibitors of
30 sterol biosynthesis including C-14 demethylation inhibitors such as triazoles which

have a 1,2,4-triazole group attached through the 1-nitrogen to a large lipophilic group, in particular triadimefon, propiconazole, tebuconazole, cyproconazole and tetraconazole along with flusilazole which incorporates a silicon atom, myclobutanil, flutriafol and imibenconazole. Other fungicides which can be used include RNA
5 biosynthesis inhibitors, phospholipid biosynthesis inhibitors, melanin biosynthesis inhibitors, fungal protein biosynthesis inhibitors and cell wall biosynthesis inhibitors.

The compositions of the present invention can be in liquid or solid form. Liquid compositions can be aqueous or non aqueous while solid forms include powders or dusts, granules and tablets. For rodenticides, in particular, the
10 compositions can take the form of a bait, especially a foodstuff, for example grain, which has been treated with the rodenticide and the special oxide.

The concentration of the active ingredient in the composition can vary within a wide range but is typically 0.5 to 95, for example 1 to 50, % by weight.

A composition according to the invention preferably contains from 0.5% to
15 95% by weight (w/w) of active ingredient.

The compositions for agricultural or horticultural use according to the invention generally contain a carrier to facilitate application to the locus to be treated, which may for example be a plant, seed or soil, or to facilitate storage, transport or handling. The carrier may be a solid, or a liquid, as well as material which is
20 normally a gas but which has been compressed to form a liquid.

The compositions may be in the form of, for example, emulsion concentrates, solutions, oil in water emulsions, wettable powders, soluble powders, suspension concentrates, dusts, granules, water dispersible granules, micro-capsules and gels. Other substances, such as fillers, solvents, solid carriers, surface active compounds
25 (surfactants), and optionally solid and/or liquid auxiliaries and/or adjuvants can be present. The composition can be formulated for dispersing by, for example, spraying, atomizing, dispersing or pouring.

Solvents which may be used include aromatic hydrocarbons, e.g. substituted naphthylenes, phthalic acid esters such as dibutyl or dioctyl phthalate, aliphatic
30 hydrocarbons, e.g. cyclohexane or paraffins, alcohols and glycols as well as their

ethers and esters, e.g. ethanol, ethyleneglycol mono- and dimethyl ether, ketones such as cyclohexanone, strongly polar solvents such as N-methyl-2-pyrrolidone or γ -butyrolactone, higher alkyl pyrrolidones, e.g. n-octylpyrrolidone or cyclohexylpyrrolidone, epoxidized plant oil esters, e.g. methylated coconut or soybean oil ester and water. Mixtures can also be used.

Solid carriers, which may be used for dusts, wettable powders, water dispersible or other granules, and granules or other particles that include mineral fillers, such as silicas, calcite, talc, kaolin, montmorillonite or attapulgite. The physical properties may be improved by addition of highly dispersed silica gel or polymers. Carriers for granules may be porous material, e.g. pumice, kaolin, sepiolite, bentonite; non-sorptive carriers may be calcite or sand.

The compositions can be formulated as concentrates which can subsequently be diluted by the user before application. The presence of small amounts of a carrier which is a surfactant facilitates this process of dilution. Thus, preferably the compositions according to the invention preferably contain a surfactant. For example, the composition may contain two or more carriers, at least one of which is a surfactant. Such surfactants may be nonionic, anionic, cationic or zwitterionic.

The compositions of the invention may for example be formulated as wettable powders, water dispersible granules, dusts, granules, solutions, emulsifiable concentrates, emulsions, suspension concentrates and aerosols. Wettable powders usually contain 5 to 90% w/w of active ingredient and 3 to 10% w/w of dispersing and/or wetting agent and, where desirable, 0 to 10% w/w of stabilizer(s) and/or other additives such as penetrants or stickers. Dusts are usually formulated as a dust concentrate having a similar composition to that of a wettable powder but without a dispersant. Water dispersible granules are usually prepared to have a size from 0.15 mm to 2.0 mm and contain 0.5 to 90% w/w active ingredient and 0 to 20% w/w of additives such as stabilizers, surfactants, slow release modifiers and binding agents. Emulsifiable concentrates usually contain, in addition to a solvent or a mixture of solvents, 1 to 80% w/v active ingredient, 2 to 20% w/v emulsifiers and 0 to 20% w/v of other additives such as stabilizers, penetrants and corrosion inhibitors. Suspension

concentrates usually contain 5 to 75% w/v active ingredient, 0.5 to 15% w/v of dispersing agents, 0.1 to 10% w/v of suspending agents such as protective colloids and thixotropic agents, 0 to 10% w/v of other additives such as defoamers, corrosion inhibitors, stabilizers, penetrants and stickers, and water or an organic liquid in which
5 the active ingredient is substantially insoluble; certain organic solids or inorganic salts may be present dissolved in the formulation to assist in preventing sedimentation and crystallization or as antifreeze agents for water.

The following Example further illustrates the present invention.

10 **Acid Extraction of Manganese Doped Titania**

Samples of manganese doped titania were soaked in 25% hydrochloric acid for various times at room temperature. The titania was settled by centrifugation and the supernatant liquid transferred to a 50ml volumetric flask. The titania was washed once by re-suspension in water with the aid of ultrasonics and again centrifuged. The
15 washings were added to the volumetric flask and the contents made to 50 ml. with de-ionised water.

Samples of the extracts, together with the original powder samples, were analysed for manganese. The water extracts were analysed directly by Atomic Absorbtion Spectroscopy (AAS). The powders were similarly analysed, after
20 digestion with a hydrofluoric acid-sulphuric acid mixture.

DPPH (Radical Scavenging) Assay.

A stock solution of 1mM DPPH in MeOH was made. Samples containing 120µl of DPPH (1mM) plus 300µl TiO₂ (3 mg/ml) were made up to 3ml with MeOH
25 and were placed in a 10 mm quartz cuvette. DPPH is a stable radical, which absorbs at 520nm, therefore a loss of absorbance at this wavelength, is a measure of the radical scavenging ability of the TiO₂. The titania samples were taken from the above series of extractions. The samples were kept in the dark and the absorbance at 520 nm measured every 5 minutes. The samples required mixing before each
30 measurement was taken in order to redisperse the TiO₂.

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Time of exposure (hrs)	Extracted Mn (%)	Rate of loss of DPPH (mAbs/min)
0	0	3.4
0.25	3.22	2.05
1.5	4.58	1.6
48	26.0	0.35

10 It is clear from these data that 74% of the manganese remained after 48 hours.
As the rate of loss of DPPH is then very small it is clear that it is the remaining 26%
of the manganese which is in or on the surface which acts to scavenge free radicals.
Thus particles having manganese available at the surface will scavenge free radicals.

CLAIMS

1. A composition suitable for veterinary, agricultural or horticultural use which comprises at least one organic veterinarily, agriculturally and/or
5 horticulturally active compound, and titanium dioxide and/or zinc oxide which has been doped at least in or on a surface thereof with one or more other elements.
2. A composition suitable for household use which comprises at least one organic biocide, and titanium dioxide and/or zinc oxide which has been doped at least in or on a surface thereof with one or more other elements.
- 10 3. A composition according to claim 1 or 2 wherein the dopant is manganese, selenium, cerium, chromium, vanadium or iron.
4. A composition according to claim 3 wherein the dopant is manganese.
5. A composition according to any one of the preceding claims wherein the dopant is present in an amount from 0.05 % to 10 mole %.
- 15 6. A composition according to claim 5 wherein the dopant is present in an amount from 0.5 to 2 mole % by weight.
7. A composition according to any one of the preceding claims which comprises doped titanium dioxide.
8. A composition according to any one of the preceding claims wherein
20 the titanium dioxide is in rutile form.
9. A composition according to claim 1 or 2 which contains reduced zinc oxide.
10. A composition according to any one of the preceding claims which comprises 0.5 to 20 mole % by weight of the oxide.
- 25 11. A composition according to any one of the preceding claims wherein the oxide has a particle size from 1 to 200 nm.
12. A composition according to any one of the preceding claims wherein the active compound is a herbicide, fungicide, insecticide, acaricide, miticide or rodenticide.

13. A composition according to claim 12 wherein the active compound is an insecticide.

14. A composition according to any one of the preceding claims which contains one or more of a filler, organic solvent or surfactant.

5 15. A composition according to any one of the preceding claims which is in the form of an aqueous or non-aqueous liquid, a powder, granules or tablet.

16. A composition according to claim 1 or 2 substantially as hereinbefore described.

10 17. Use of a surface doped TiO_2/ZnO as defined in any one of claims 1 to 9 to reduce the concentration of one or more veterinarily, agriculturally and/or horticulturally active compounds in a composition suitable for veterinary, agricultural, horticultural or household use.

15 18. Use of a surface doped TiO_2/ZnO as defined in any one of claims 1 to 9 to increase the shelf life of one or more veterinarily, agriculturally and/or horticulturally active compounds in a composition suitable for veterinary, agricultural, horticultural or household use.

20 19. A method of increasing the effectiveness of a composition suitable for veterinary, agricultural, horticultural or household use which comprises one or more organic veterinarily, agriculturally or horticulturally or household active compounds, which comprises incorporating into the composition a surface doped TiO_2/ZnO as defined in any one of claims 1 to 9.

20. A method for treating an agricultural or horticultural species at a locus which comprises treating the locus with a composition as claimed in any one of claims 1 to 16.

ABSTRACT
IMPROVED AGRICULTURAL COMPOSITIONS

A composition suitable for veterinary, agricultural or horticultural use is
5 disclosed which comprises at least one organic veterinarally, agriculturally and/or
horticulturally active compound, and titanium dioxide and/or zinc oxide which has
been doped at least in or on its surface with a second element as well as a
composition suitable for household use which comprises at least one organic biocide
and one of the specified oxides.

